Experimental and Theoretical Studies of the Reactions of Electrophiles with Cationic Formyl Complexes; Formation of Methoxy- and Hydroxy-carbene Complexes of Ruthenium(II) and Osmium(II)

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Complexes of the form *trans*-[M(CHO)(CO)(P–P)$_2$][SbF$_6$] [M = Ru or Os, P–P = Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe) or *o*-(Ph$_2$P)$_2$C$_6$H$_4$ (dppb)] react with CF$_3$SO$_3$R (R = Me or H) at −30 °C to give *trans*-[M(CHOR)(CO)(P–P)$_2$][SbF$_6$][CF$_3$SO$_3$], which have been isolated and spectroscopically characterised. EHMO (extended Hückel molecular orbital) calculations demonstrate that the site of attack for hard or soft electrophiles is expected to be the formyl oxygen atom (as is observed) but that hard nucleophiles will attack the carbonyl carbon atom and soft nucleophiles the formyl carbon atom.

We have been carrying out[1–7] extensive studies of ruthenium and osmium complexes containing reduced CO fragments (especially formyl) with a view to modelling intermediates and fundamental reaction steps involved in the catalytic hydrogenation of carbon monoxide. Ruthenium based complexes are important homogeneous catalysts for the production of oxygenates (methanol, ethanol, and 1,2-dihydroxyethane) from CO–H$_2$.[8,9]

It is generally agreed that formyl is the first important intermediate in these reactions, although we[6] and others[9] have recently provided evidence that this may be formed by an intermolecular rather than an intra-molecular hydride-transfer reaction. The next step of the reaction has generally been assumed to be the formation of free or bound methanal by reductive coupling of formyl and hydride.[9,10]

Since the ruthenium and osmium formyl complexes that we have prepared by attack of hydride on [M(CO)$_2$(P–P)$_2$]$^{2+}$ [M = Ru or Os, P–P = bis(diphenylphosphino)methane, dppm, (*cis*); 1,2-bis(diphenylphosphino)ethane, dppe, (*trans*); or 1,2-bis(diphenylphosphino)benzene, dppb, (*trans*)], are all cationic, we have made several attempts to reduce these species by further attack of hydride. In general, we have failed to observe any reaction, although we have some n.m.r. evidence[2] for the possible formation of *cis*-[Os(CHO)$_2$(dppm)$_2$].

We now report that, despite the positive charge on the formyl complexes, the formyl groups display significant nucleophilic character and are readily attacked by electrophiles. Very similar reactivity has been observed by Lilga and Ibers[11] for the isoelectronic iridium(III)–formyl complex, *trans*-[IrH(CHO)(dppe)$_2$]$^+$ and there is both theoretical[12] and experimental[13] evidence that the neutral [Re(η-C$_5$H$_5$)(NO)(PPh$_3$)(CHO)] reacts with H$^+$ to give [Re(η-C$_5$H$_5$)(NO)(PPh$_3$)(CHOH)]. A preliminary report of our results has appeared.[14]

Results and Discussion

Synthetic Studies.—Reactions of *trans*-[M(CHO)(CO)(P–P)$_2$][SbF$_6$] (M = Ru or Os, P–P = dppe or dppb) with excess CF$_3$SO$_3$R (R = H or Me)* as sources of R$^+$ at −30 °C produce colourless solutions from which complexes analysing (Table 1) as [M(CHOR)(CO)(P–P)$_2$]X (X is a 1:1 mixture of [SbF$_6$]$^-$ and [CF$_3$SO$_3$]$^-$) can be isolated in high yield. ^{1}H N.m.r. studies (Table 2) show that resonances from the formyl proton (δ *ca.* 15 p.p.m.) are replaced by new resonances in the low-field region of the spectrum. In all cases there is a binomial quintet in the region δ *ca.* 10–12 p.p.m. and for related pairs of molecules, the carbene proton resonates 1–2 p.p.m. to lower frequency for the methoxycarbene complex than for the hydroxycarbene. The carbene proton resonances of other reported methoxy- and hydroxy-carbenes generally have chemical shifts in this region.[11,13,15–17] For the hydroxycarbene complexes, resonances from the OH proton are not observed in the high frequency region, perhaps suggesting rapid intermolecular exchange of H$^+$.

Table 1. Microanalytical data for new carbene complexes*

Compound	Found (calc.) (%) C	H	P
[Ru(CHOMe)(CO)(dppe)$_2$]X	49.3 (49.6)	4.2 (3.8)	9.2 (9.2)
[Ru(CHOMe)(CO)(dppb)$_2$]X	53.9 (53.0)	4.0 (3.6)	
[Ru(CHOH)(CO)(dppb)$_2$]X	53.1 (52.7)	3.8 (3.5)	8.9 (8.6)
[Os(CHOMe)(CO)(dppe)$_2$]X·CH$_2$Cl$_2$	43.8 (44.7)	3.7 (3.5)	8.2 (8.1)
[Os(CHOH)(CO)(dppe)$_2$]X·CH$_2$Cl$_2$	44.1 (44.3)	3.4 (3.5)	8.2 (8.2)
[Os(CHOMe)(CO)(dppb)$_2$]X·CH$_2$Cl$_2$	48.0 (48.0)	3.4 (3.3)	8.0 (7.6)
[Os(CHOH)(CO)(dppb)$_2$]X·CH$_2$Cl$_2$	47.1 (47.7)	3.4 (3.2)	7.4 (7.7)

* All complexes have *trans* stereochemistry; X is SbF$_6$–CF$_3$SO$_3$ (1:1); CH$_2$Cl$_2$ is identified in the ^{1}H n.m.r. spectra of all the osmium complexes, measured in CD$_3$NO$_2$.

A singlet in the ^{31}P n.m.r. spectrum of each complex (Table 2) confirms that the *trans* stereochemistry is conserved, whilst in each case the resonance is at a lower frequency than that of the formyl and close to the position of the resonance from the analogous dicarbonyl dication,[2,7,18] suggesting the expected electronic similarity between the two dicationic species.† This electronic similarity is further exemplified by the high values of ν(C=O) (2 010—2 040 cm^{-1}), which are very similar to those observed for the dicarbonyl dications. Broad ν(O–H) bands near 3 550 cm^{-1} are observed for the hydroxycarbene complexes (Table 2).

Monitoring the reactions by ^{31}P n.m.r. spectroscopy shows that they proceed quantitatively within the time of mixing and accumulating the spectra (*ca.* 5 min) at −30 °C. As with the ruthenium–formyl[3,7] complexes, the carbene complexes decompose on warming to room temperature to give [RuH(CO)(P–P)$_2$]$^+$. Although the mechanism of this reaction is unknown,

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* Unlike [Re(η-C$_5$H$_5$)(NO)(PPh$_3$)(CHO)],[13] the cationic osmium and ruthenium formyls do not react with CF$_3$CO$_2$H, perhaps suggesting a slightly lower nucleophilicity consistent with the excess positive charge.

† Incorrect signs are given to the ^{31}P chemical shifts in ref. 18.

Table 2. Selected spectroscopic data for new carbene complexes

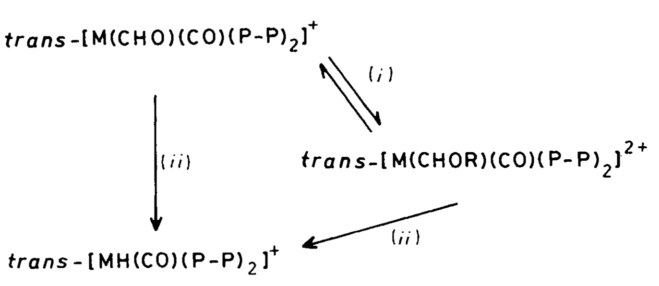
	N.m.r./p.p.m. (Hz)*			I.r. $\nu_{max.}$/cm^{-1}	
		^{1}H			
	^{31}P	C*H*O	OCH_3	ν(C=O)	ν(O–H)
$[Ru(CHOH)(CO)(dppb)_2]^{2+}$	53.4 (s)	10.5 (qnt, 6)		2 010	3 550br
$[Ru(CHOMe)(CO)(dppb)_2]^{2+}$	52.1 (s)	9.7 (qnt, 5.5)	3.8 (s)	2 025	
$[Ru(CHOMe)(CO)(dppe)_2]^{2+}$	44.1 (s)	10.6 (qnt, 6)	3.7 (s)	2 020	
$[Os(CHOH)(CO)(dppb)_2]^{2+}$	23.8 (s)	11.8 (qnt, 6)		2 020	3 525br
$[Os(CHOH)(CO)(dppe)_2]^{2+}$	16.8 (s)	12.3 (qnt, 5.5)		2 040	3 525br
$[Os(CHOMe)(CO)(dppb)_2]^{2+}$	21.1 (s)	10.2 (qnt, 6)	3.6 (s)	2 040	
$[Os(CHOMe)(CO)(dppe)_2]^{2+}$	15.1 (s)	11.1 (qnt, 5.5)	3.7 (s)	2 040	

* In CH_2Cl_2 at −30 °C.

Table 3. EHMO parameters

Orbital		H_{ii}/eV	ζ_1	ζ_2	C_1*	C_2*	Ref.
H	1*s*	−13.6	1.30				22
C	2*s*	−21.4	1.625				22
	2*p*	−11.4	1.625				
O	2*s*	−32.4	2.275				23
	2*p*	−14.8	2.275				
P	3*s*	−18.6	1.60				22
	3*p*	−14.0	1.60				
	3*d*	−7.0	1.60				
Ru	4*d*	−14.9	5.38	2.30	0.5343	0.6368	21
	5*s*	−10.4	2.08				
	5*p*	−6.87	2.04				
Os	5*d*	−10.95	5.57	2.42	0.6372	0.5598	24
	6*s*	−8.49	2.45				
	6*p*	−3.48	2.43				

* Coefficient in double-zeta expansion.



Scheme. Reaction of electrophiles with *trans*-$[M(CHO)(CO)(P–P)_2]^+$; (*i*) $CFSO_3R$ (R = Me or Et), CH_2Cl_2, −30 °C; (*ii*) room temperature. M = Ru

it may also suggest that the attack of R^+ on the formyl complexes is reversible. These reactions are outlined in the Scheme.

Detailed studies[3,7] of the decomposition reactions of *trans*-$[M(CHO)(CO)(P–P)_2]^+$, which give $[MH(CO)(P–P)_2]^+$ at room temperature, show that the formyl complexes are indefinitely stable in solution at −30 °C. It is therefore of particular interest that the reactions with electrophiles (H^+ or Me^+) occur at −30 °C suggesting that, at least for these complexes the formyl intermediates are trapped by electrophiles more readily than they decompose. It is possible, therefore, that in catalytic systems for carbon monoxide hydrogenation, unstable formyl intermediates, formed by intermolecular hydride transfer,[6,9] may undergo protonation at a rate faster than their decomposition.

Table 4. Net atomic charges calculated for carbon and oxygen in $[M(CHO)(CO)(PH_3)_4]^+$

	M = Ru		M = Os	
	cis	*trans*	*cis*	*trans*
Carbonyl ligand				
q(C)	+1.17	+1.17	+0.54	+0.58
q(O)	−0.82	−0.82	−0.86	−0.68
Formyl ligand				
q(C)	+0.89	+0.83	+0.46	+0.42
q(O)	−1.00	−1.03	−1.05	−1.06

EHMO Calculations.—Although attack by electrophiles on cationic formyl complexes is at first sight surprising, EHMO (extended-Hückel molecular orbital) calculations[19,20] on the simple models *cis*- and *trans*-$[M(CHO)(CO)(PH_3)_4]^+$ (M = Ru or Os), using published atomic parameters[21–24] (see Table 3) and geometrical parameters based upon those found[1,2] by *X*-ray analysis for *trans*-$[Ru(CDO)(CO)(dppe)_2]^+$ and *trans*-$[Os(CHO)(CO)(dppe)_2]^+$ provide a straightforward mechanistic rationalisation.

The net atomic charges for the carbon and oxygen atoms of the carbonyl and formyl ligands (Table 4) show that for both *cis* and *trans* isomers, and for both ruthenium and osmium, the oxygen atom of the formyl ligand is more negatively charged than that in the carbonyl ligand, but the more positively charged of the two carbon atoms is that in the carbonyl ligand. Hence for charge-controlled reactions, it is to be expected that electrophilic reagents will attack the formyl oxygen, but nucleophilic reagents will attack the carbonyl carbon.

On the other hand, the highest occupied molecular orbital (h.o.m.o.) for each of the ruthenium complexes and the highest occupied ligand orbital for the osmium complexes is a lone-pair orbital concentrated on the formyl {as found,[12] for example, in $[Re(\eta\text{-}C_5H_5)(NO)(PPh_3)(CHO)]$} so that in orbital-controlled reactions also, electrophiles will be expected to attack the formyl oxygen in preference to the carbonyl oxygen.

The lowest unoccupied ligand orbital is, in every case, distributed over both the carbonyl and formyl C–O fragment but the formyl component dominates: thus in the *trans* ruthenium complex, the coefficients for this orbital for the formyl group are: C, +0.79, O, −0.46; and for the carbonyl group are: C, +0.31; O, −0.18. Hence, in contrast to charge-controlled nucleophilic addition which is expected to occur at the carbonyl ligand, orbital-controlled nucleophilic addition is to be expected at the formyl ligand. Thus while both hard and soft electrophiles are expected to attack at the formyl ligand, hard nucleophiles will attack at the carbonyl and soft nucleophiles at the formyl. Our failure to observe attack of hydride on $[M(CHO)(CO)(P\text{–}P)_2]^+$ perhaps arises from a slow rate of attack of H^- rather than from any thermodynamic barrier to such an attack.

Experimental

The synthetic work reported here was carried out in the School of Chemistry, University of Liverpool.

Microanalyses were by Elemental Microanalysis Ltd. and the University of Liverpool Microanalytical Service. Infrared (i.r.) spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 577 grating spectrometer and n.m.r. spectra on a Bruker Associates WM 250 spectrometer, operating in the Fourier-transform mode with (for ^{31}P) proton noise decoupling.

All solvents were dried before use by distillation from CaH_2 (CH_2Cl_2 and $MeNO_2$) or sodium diphenylketyl [diethyl ether and light petroleum (b.p. 40—60 °C)]. All reactions were carried out under nitrogen using standard Schlenk-line and catheter tubing techniques.

Formyl complexes were prepared by previously published procedures,[1,2,7] whilst CF_3SO_3R were obtained commercially and used without further purification.

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*carbonyl*(*methoxycarbene*)*ruthenium*(II) *Hexafluoroantimonate Trifluoromethanesulphonate*.—The complex *trans*-$[Ru(CHO)(CO)(dppe)_2][SbF_6]$ (0.1 g) was dissolved in CH_2Cl_2 (10 cm^3) at −30 °C and treated with CF_3SO_3Me (0.1 cm^3). The resulting colourless solution was stored at −30 °C for 4 h before filtration into light petroleum–diethyl ether (1:1, 50 cm^3) pre-cooled to −30 °C. The resulting white solid was collected, washed with light petroleum (50 cm^3), and dried *in vacuo* (yield *ca.* 60%). ^{31}P N.m.r. evidence suggested that this compound was contaminated with *trans*-$[RuH(CO)(dppe)_2][SbF_6]$.

The following new compounds were similarly prepared but precipitation was from the solvents shown. *trans*-$[Ru(CHOMe)(CO)(dppb)_2][SbF_6][CF_3SO_3]$, diethyl ether–light petroleum (1:1, 75 cm^3); *trans*-$[Ru(CHOH)(CO)(dppb)_2][SbF_6][CF_3SO_3]$,* diethyl ether (100 cm^3); *trans*-$[Os(CHOMe)(CO)(dppe)_2][SbF_6][CF_3SO_3]\cdot CH_2Cl_2$, light petroleum (50 cm^3); *trans*-$[Os(CHOH)(CO)(dppe)_2][SbF_6][CF_3SO_3]\cdot CH_2Cl_2$,* diethyl ether–light petroleum (1:1, 100 cm^3); *trans*-$[Os(CHOMe)(CO)(dppb)_2][SbF_6][CF_3SO_3]\cdot CH_2Cl_2$, diethyl ether–light petroleum (1:1, 60 cm^3); *trans*-$[Os(CHOH)(CO)(dppb)_2][SbF_6][CF_3SO_3]\cdot CH_2Cl_2$, light petroleum (100 cm^3).

The first crop of crystals of $[Os(CHOH)(CO)(dppb)_2][SbF_6][CF_3SO_3]$ was contaminated with the starting formyl complex but a second crop (*ca.* 20%), obtained on standing at −30 °C for 2 weeks, was spectroscopically and analytically pure.

Similar reactions carried out using trifluoroethanoic acid in place of trifluoromethanesulphonic acid were unsuccessful, unreacted formyl complex being recovered in all cases.

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* Contaminated with up to 15% of unreacted formyl complex.